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Original Article

Concentration of heavy metals in drinking water of Hawassa Zuria Woreda, Sidama Region, Ethiopia

Yohannes Seifu Berego[1*], Solomon Sorsa Sota[1], Mihret Dananto Ulsido[2], Embialle Mengistie Beyene[3], Amanuel Ejeso Debiso[3]

[1] Department of Biology, Hawassa University, Hawassa, Sidama Region, Ethiopia; [2] Department of Water Resource Engineering and Management, Graduate School of Water Resource and Irrigation Engineering, Hawassa University, Hawassa, Sidama Region, Ethiopia; [3] Department of Environmental Health, College of Medicine and Health Sciences, Hawassa University, Hawassa, Sidama Region, Ethiopia

[*]Correspondence: Yohannes Berego; E-mail: johnseifu80@gmail.com

Abstract

Background. Access to safe drinking water across the globe remains a major public health concern. Hawassa Zuria Woreda faces the same problem of lack of drinking water as other neighboring districts. The main aim of this study was to determine the levels of heavy metals such as Mn, Pb, Zn, Co, Cu , Ni and Fe in drinking water Hawassa Zuria Woreda, Sidama Region, Ethiopia.

Methods. A total of fifteen representative water samples were collected randomly from different sources such as two samples from the source (BoreHole), five samples from reservoir, and eight samples from taps. Acid cleaned one-liter polyethylene bottles were used to collect samples from the selected water sources, which were then evaluated for seven trace elements (Mn, Pb, Zn, Co, Cu, Ni and Fe).This was determined using Flame Atomic Absorption Spectroscopy (Buck Scientific, Model 210VGP AAS, USA) equipped with deuterium background corrector and used air acetylene flame atomizer.

Results. The results of the physical analysis were in the following range; pH, 6.69 to 7.65; temperature, 20 to 26^{o}c; electric conductivity, 468.67 to 809.33µS/cm; turbidity, 1.2 to 11.63mg/l; and TDS, 281.2 to 485.60 mg/l. Concentrations of essential trace metal (Cu, Fe, and Zn) were below the guideline values of WHO and Ethiopian standard. Manganese and lead surpassed standard values of WHO and Ethiopian standard in 40% (n=6) in each case. Calculated values of pollution index for Mn, Zn, Fe and Cu were well below 1, which implies that the water samples were not polluted and are safe for drinking, whereas pollution index for Pb (Sample 1, Sample 2, and Sample 11) which was contaminated with lead and for Ni (Sample 4, Sample 8, and Sample 10) which was contaminated with Nickel. Overall six out of the fifteen samples indicated lead and nickel contamination. The mean HPI and HEI were 75.72 and 1.47, respectively. The mean HPI value did not surpass the critical value of 100. The distribution of average metal concentrations in the drinking water was found in the order of Zn>Ni>Co>Cu>Mn>Fe> Pb. One sample t-test revealed that highly significant difference (p<0.01) was observed between the guideline values of WHO and the metals except the lead. Correlation analysis further revealed that the elemental pair Pb/Zn ($r = 0.524$, $P < 0.05$) is significantly correlated with each other, whereas the rest of elemental pairs show no significant correlation with each other. Element and physicochemical associations show the pair Pb/turbidity($r = 0.715$, $P < 0.01$) is correlated with each other. Similarly, Cu/pH($r = 0.555$, $P < 0.05$) and Cu/Turbidity ($r = -0.522$, $P < 0.01$) are significantly correlated with each other. Likewise, EC/turbidity ($r = 0.567$, $P < 0.05$) is significantly correlated with each other.

Conclusion: This study strongly suggests that the authorized body pay special attention to physico-chemical approaches for removing nickel and lead from water, such as chemical coagulation, chemical oxidation or reduction, active carbon adsorption, filtration, ion exchange, and membrane technologies.

Keywords: Drinking water, Heavy Metals, Water pollution index, Ethiopia

Introduction

Water is vital to sustain life, and a reasonable (adequate, safe and accessible) supply of drinking water should be available to all (1-3). Globally, access to safe drinking water remains a major public health concern. Providing access to safe drinking-water can result in noticeable benefits to health. Every effort should be made to obtain the safest drinking water possible. (2). The availability and accessibility of good quality drinking water plays the greatest role in both social and economic development and it is a basic factor in guaranteeing public health, the protection of the environment and sustainable development (4).Water is one of the most vital and valuable natural resources. It is vital to man's existence and without it, there would be no life on earth (5). However, the majority of the world's populations without access to improved water supply or sanitation services live in developing regions mainly in Africa and Asia (6). Globally, 2 million children die annually because of lack of potable water and basic sanitation, and millions of women and young girls are forced to spend hours in fetching and carrying water. In 2019, 1 in 3 people globally did not have access to safe drinking water (around 33.3 per cent of the world population) (6).

Heavy metals are a metallic, stable element with a high atomic weight and a density at least five times that of water. Even at very low concentrations, they are highly toxic and can cause damaging effects (7). Heavy metals are among the most public environmental pollutants, and their occurrence in waters and biota indicate the presence of natural or anthropogenic sources (7). Heavy metals tend to accumulate in human organs and nervous system and interfere with their normal functions (8). Manganese(Mn), lead(Pb), zinc(Zn), cobalt(Co), copper(Cu), and nickel(Ni) are heavy metals that have garnered a lot of attention in recent years because they create health problems (2).

A number of studies have been conducted in the world to determine the concentration of heavy metals in water samples (5, 10-16). Among these heavy metals Zn , Pb, As, Cd and Cu are present throughout the earth crust and are much toxic than other metals. These toxic heavy metals have a tendency to accumulate in the body and may result in chronic damages(17). Currently, in developing countries, there has been an increasing health related concern associated with the quality of drinking water. According to WHO/UNICEF (2017), Globally, around 159 million people still collect drinking water right from surface water sources; from these, 58% of them lived in sub-Saharan Africa and around 844 million people still lacked even a basic drinking water service due largely to microbiological and chemical contaminations(6).

Developing countries are under increasing threat of drinking water sources from contaminations by chemical, physical and microbial pollutants (15). According to report from Hawasssa zuria Health office (2012), about 75% of patients suffer from water borne diseases like, stomach ache, diarrhea, vomiting, high fever and gastrointestinal distress. As far as the researchers know, no assessment of the physicochemical qualities of drinking water has been conducted in Hawassa Zuria Woreda. There are mining activities close to bore holes and also intensive farming practices through application of organic fertilizers, minerals and pesticides to the agricultural soil that contribute to serious levels of heavy metals in the water bodies and farmers introduce livestock within the field where water sources are available. These situations may cause contamination of water sources. Therefore the main aim of this study was to determine the levels of heavy metals such as Mn, Pb, Zn, Co, Cu and Ni in drinking water of Hawassa Zuria Woreda, Sidama Region, Ethiopia.

Materials and Methods

Description of the Study Area

This study was carried out in a rural area in Hawassa Zuria Woreda, Ethiopia. Geographic location of the woreda is between 07° 01′ 54″ to 07° 50′ 36″ N and 38° 15′ 39″ to 38° 25′ 43″ E. The capital town of Hawassa Zuria woreda is Dore Bafano, which is located 21 km SE from Hawassa. It borders Boricha district in the south, Tula town in the east, Lake Hawassa in the north, the Oromia region in the west. The altitudinal range is 1700 m to 1850 m.a.s.l. The Woreda is divided into 23 peasant administrations. Maize is the dominant crop produced in the woreda. In 2019 total population of the woreda was 160,180; among these 81692(51%) were females and 78488(49%) were males. The woreda has 4 public health centers, 23 health posts, 1 Primary hospital, and 8 private clinics.

Hawassa zuria wereda is the study area and the location experiences annual mean maximum and minimum temperatures of 30 °C and 17 °C, respectively, and the mean annual rainfall is 1015 mm. There are two agro-ecologic conditions comprising of 80% “kola” (lowland), 20% “woyna dega” (midland) (18).

In the study area, two boreholes are used for obtaining drinking water. The water collected from the boreholes is then stored in two large reservoirs near Betemengist. More than 160,000 people rely on the use of groundwater. The treatment process being applied is chlorination alone.

Sampling technique

For this study, out of the 23 rural Kebele Administrations in Hawassa Zuria Woreda, only 20% were selected, due to availability (purposively) of the different types of water sources for drinking purposes. Drinking water quality analyses usually cover the sources, the reservoir (disinfection point) and tap (point of use). As a result, water samples were taken from the reservoir(R) and borehole (BH). In addition, water samples were collected from piped water at selected individual taps using clean and/or sterilized containers for heavy metal.

Accordingly, five Kebeles namely Dore Bafano, Galo Argisa, Jarra Dado kebele and Rukessa Suke were selected for this purpose. Minimum sampling frequency for drinking water in the distribution system was based on the number of population served (ESA, 2013). According to Ethiopian Standard (2013) for a population range from 5,000-100,000 one sample per 5,000 populations is recommended. Finally, households from each sampled kebele were chosen using probability proportional to size sampling procedures (Table 1).

A total of fifteen representative water samples were collected from different sources such as two samples from the source (Bore Hole), five sample from reservoir, and eight samples from the Taps. Totally, fifteen samples were taken to evaluate the level of heavy metal in drinking water (Figure 1). All the studied laboratory results were compared with the Ethiopian standards and WHO guideline for drinking water quality and interpreted in accordance with the results obtained.

Sample analysis

Onsite analysis of the physical parameters such as temperature, electrical conductivity, pH, TDS and turbidity were carried out at the site of sample collection according to the standard protocols and methods of APHA(19). The pH and temperature was measured using pH meter (H1 8014 HANNA Instrument). Before taking the measurements, the pH meter were calibrated, with three standard solutions (pH 4.0, 7.0, and 10.0) and the value of each sample was taken after submerging the pH probe in the water sample and holding for a couple of minutes to achieve a stabilized reading. After the measurement of each sample, the probe was rinsed with deionized water to avoid cross contamination among different samples.

The conductivity of water was determined with the aid of Conductivity meter and articulated in terms of µS/cm. The probe was calibrated using a standard solution with a known conductivity. The probe was submerged in the water sample and the reading was recorded after the disappearance of stability indicator. After the measurement of each sample, the probe was rinsed with deionized water to avoid cross contamination among different samples.

Table 1: Number of people and sample frequency for household and tap water sampling

Kebeles	Population	Number of samples	
		Taps	Community Reservoir
Dore Bafano	9102	2	1
Galo	8301	2	1
Jarra Dado	9688	2	1
Umbulo Kajima	6111	1	1
Rukessa Suke	4913	1	1
Total	29,115	8	5

The turbidity of water sample was directly determined by the portable turbidity meter (Jenway 6035) at room temperature. Each sample was poured in the sample holder and kept inside for a few minutes. After achieving the reading stability, the value was recorded. Their measurements were taken immediately after the samples were collected on each site. Total Dissolved Solids (TDS) were determined by multiplying through the conductivity value. The conductivity of the sample was determined and the value multiplied by 0.6 to get the TDS. TDS = Conductivity x 0.6 (3). For each sampling site, samples were collected in 1000ml polyethylene plastic bottles for trace metal analysis from sampled water supply schemes and acidified and preserved with HNO_3. Water sampling and preservation techniques followed the standard

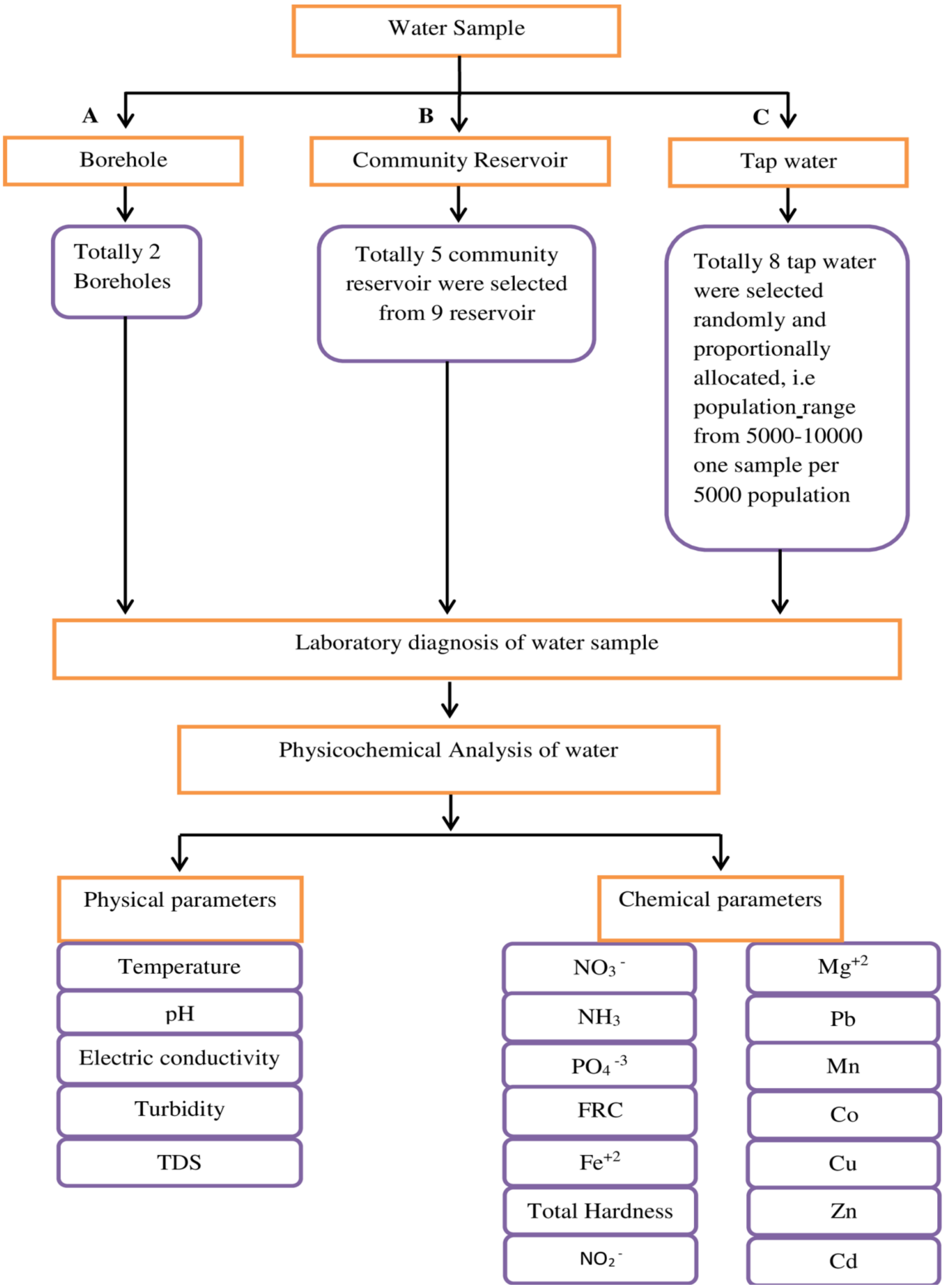

Figure 1: Flowchart of the study design. Three different type of water were collected (A) Borehole, (B) Reservoir, (C) Tap water.

methods of water sampling and preservation (19). Before collection, bottles were washed with concentrated nitric acid and distilled water to avoid contamination. The samples were collected three times a day (at 3-hr interval) for six consecutive days. The samples were taken in the morning between 7.00 and 8.00 a.m.

The samples collected for the heavy metals analysis were immediately preserved to a pH value 1.5 with concentrated HNO_3 (19). The method of preparation, collection, and preservation was similar to those reported in previous studies (5, 9, 16, 20, 21). Heavy metals were analyzed at the Department of Chemistry, Hawassa University.

Heavy Metal Analysis Methods

Mn, Pb, Zn, Co, Cu and Ni were determined using Flame Atomic Absorption spectroscopy (Buck Scientific, Model 210VGP AAS, USA) equipped with deuterium background corrector and used air acetylene flame atomizer. Stock standard solutions (Buck Scientific purographics calibration standards, USA) containing 1000 mg/L of the metals Mn, Pb, Zn, Co, Cu and Ni from which 10 mg/L of intermediate standard obtained were used for preparation of calibration standards of each metal.

Instrument Operating Conditions and Calibration

A total of six metals for fifteen sample were analyzed using flame atomic absorption spectrophotometer with external calibration curve after the parameters such as burner and lamp alignment, slit width and wavelength adjustment were optimized for maximum signal intensity of the instrument. For each metal, the respective hollow cathode lamp was inserted into the atomic absorption spectrophotometer, and the solution was successively aspirated into the flame. All the Six metals (Mn, Pb, Zn, Co, Cu and Ni) were analyzed by absorption mode of the instrument. Iron was analyzed using photometer 7100. Three replicate determinations were carried out for each sample. The same analytical procedure was employed for the determination of elements in a total of six digested blank solutions for water samples (Table 2).

Heavy Metals Contamination Factor (Cf)

Pollution index is defined as the ratio of the concentration of individual parameter evaluated to that of recommended standard. It expresses the relative pollution contributed by each parameter. The threshold value is 1.0. A value less than 1.0 indicates no pollution has occurred whereas values greater than 1.0 shows significant level of pollution (22). The method of calculation was similar to those reported in previous studies(23, 24).

Pollution index is mathematically expressed as:

$$\text{Pollution Index} = \frac{Concentration}{Standard}$$

Standard refers to maximum admissible concentration of the ith parameter. In this study, the standard was used the same as the WHO guideline value for each metal. Hakanson (1980) defines four categories of contamination factors: $Cf < 1$ (Low contamination factor); $1 \leq Cf < 3$ (Moderate contamination factor); $3 \leq Cf < 6$ (considerable contamination factor); $Cf \geq 6$ (Very high contamination Factor) (22).

Table 2: Operating conditions of the instrument employed for each metal

Elements	Parameter				
	Wave length (nm)	Slit width (nm)	Lamp current (mA)	Energy (eV)	Instrumental detection limit (mg/l)
Mn	279.5	0.7	3.0	3.913	0.030
Pb	283.2	0.7	2.0	2.874	0.040
Zn	213.9	0.7	2.0	3.237	0.005
Co	240.7	0.2	4.5	3.106	0.050
Cu	324.7	0.7	1.5	3.938	0.005
Ni	341.7	0.2	7	2.624	0.020

Heavy Metals Pollution index (HPI)

The HPI is used to determine the aggregate influence of individual heavy metal on the overall quality of water. It is a model that rates the composite influence of individual heavy metal on the overall quality of water and developed in two steps. First, by establishing a rating scale for each selected parameter giving weightage and second, by selecting the pollution parameter on which the index is to be based. In the present model the unit weightage (Wi) was taken as a value inversely proportional to the recommended standard (S_i) of the corresponding parameter. This study used the WHO (2017) standards permissible value for drinking water, while the metals Mn, Pb, Zn, Fe, Cu and Ni were measured for the model index application. The HPI was calculated using the following equation (44-46).

$$\text{HPI} = \sum_{i=1}^{i=n}(Qi\ x\ Wi) \div \sum_{i=1}^{i=n}\text{Wi} \quad \text{….. Eq. (1),}$$

Where, Qi is the sub-index of the i^{th} parameter, Wi is the unit weight of the i^{th} parameter and n is the number of parameters considered; the sub-index (Qi) of the parameter is

$$\text{Qi} = \frac{Vi}{Si} \text{ x 100} \quad \text{…………. ………..……. Eq. (2),}$$

Where, Vi is the monitored value of metal of the i^{th} parameter and S_i the standard value.

In this study, the index was intended for the purpose of drinking water, and the permissible or critical pollution index value for drinking water is 100 (44**).**

Heavy Metal evaluation index (HEI)

The HEI, like the HPI, gives an overall quality of the water sample with respect to heavy metals, and is computed as shown in Eq. (3):

$$\text{HEI} = \sum_{i=1}^{n} \text{Hc} \div \text{Hmax} \quad \text{……………… Eq. (3),}$$

Where, Hc and Hmax are the measured value and maximum admissible concentration of the i^{th} parameter, respectively (47). In this study, the Hmax was used as the same as the WHO guideline value for each metal.

The classification scheme for HEI by Onyenmechi et al. (2020) which categorizes water into low, medium and high using the multiples of the mean index values was used. In this study, the cut-off values were: < 7.5, low; 7.5 -15, medium; and > 15, high.

Data Analysis

An analysis was done using Minitab version 16 packages and Microsoft Excel (MS Excel). Pearson correlation was employed to see statistically significant relation between trace elements and physical parameter. T-test was used to compare findings of study with WHO guidelines value. Data were presented using tables and figures.

Results

In-situ parameters of drinking water

The pH values of all the drinking water samples are found to be in the range between 6.69 and 7.65. The lowest and highest values are from samples (S1 and S2) and (S 15) respectively. Water temperature obtained from the present study ranged from 20 to 26 ^{o} C and the values of electric conductivity were recorded ranging from 468.67 to 809.33µS/cm.

The turbidity values ranged from 1.20 to 11.63 NTU (Nephelometric Turbidity Units). The maximum turbidity value in sample (S2) 11.67 NTU, followed by sample (S3) 9.46 NTU, sample (S11) 8.90NTU and the value of TDS ranged between 281.2 to 485.60 mg/l (Table 3).

The concentration of Heavy Metal in drinking water

From the result presented in Table 4, manganese, zinc, cobalt, copper and nickel were detected in most of the water samples. Copper and zinc were detected in all water samples while lead was only detected in the three samples.

Manganese was detected in 9 drinking water samples whereas in 6 samples it remained below the detection limit (Figure 2). Manganese values in the water ranged from 0 to 0.05650 mg/l. Galo tap 2 has the highest manganese concentration of 0.05650 mg/L, followed by Betemengist Reservoir 2 with 0.03931 mg/L and Rukessa tap water with 0.03275 mg/L. Dore tap 1 had the lowest concentration, with a 0.00303mg/L.

Table 3: Level of some physical parameters for drinking water samples in Hawassa Zuria Woreda, 2021

Site	pH	Temp	EC	Turbidity	TDS
1	6.69	21.07	468.67	5.73	281.20
2	6.69	20.00	809.33	11.63	485.60
3	6.80	26.00	760.67	9.46	456.40
4	6.70	25.03	486.00	2.28	291.60
5	7.24	24.90	699.00	5.44	419.40
6	6.83	25.00	609.67	5.75	365.80
7	7.08	25.00	541.67	3.63	325.00
8	6.83	25.00	512.33	4.84	307.40
9	6.70	25.67	723.33	3.57	434.00
10	7.24	24.90	654.00	5.56	392.40
11	6.65	25.67	769.33	8.90	461.60
12	6.78	25.37	495.33	4.29	297.20
13	7.08	25.00	544.00	3.63	326.40
14	7.10	25.00	543.67	3.30	326.20
15	7.65	24.07	734.00	1.28	440.40

Sample 1 =Gamato bore hole, Sample 2=Boqo BH ,Sample 3=Betemengist Reservoir 1, Sample 4=Betemengist Reservoir 2 , Sample 5= Dore bafano Reservoir, Sample 6=Dore tap 1 , Sample 7 =Dore bafano tap 2 , Sample 8 =Galo tap 1, Sample 9 =Galo tap 2 , Sample 10 =Umbulo Reservoir , Sample 11=umbulo tap , Sample 12Jara reservoir , Sample 13 =Jara tap 1 , Sample 14 =Jara tap 2 and Sample 15 =Rukessa tap water.

Table 4: Concentrations of metals (trace and heavy) determined in the water samples

Sample	Mn(mg/l)	Pb(mg/l)	Zn(mg/l)	Co(mg/l)	Cu(mg/l)	Ni(mg/l)	Fe
1	0.03020	**0.01167**	0.16433	0.05200	0.00510	0.02100	0.0
2	0.03100	**0.04833**	0.20433	0.05000	0.00525	0.02250	0.01
3	ND	ND	0.06367	ND	0.01200	0.02400	0.0
4	0.03931	ND	0.01633	0.06767	0.00633	**0.09367**	0.017
5	0.02117	ND	0.47167	0.03000	0.00583	ND	0.0
6	0.00303	ND	0.41800	ND	0.01567	ND	ND
7	ND	ND	0.25633	ND	0.04000	ND	0.0
8	ND	ND	0.14267	ND	0.01400	**0.07067**	0.0
9	0.05650	ND	0.24267	0.01367	0.02133	0.04033	0.0
10	0.01160	ND	0.30733	0.00833	0.02267	**0.09133**	0.043
11	0.03023	**0.05567**	0.96623	ND	0.01100	ND	0.033
12	ND	ND	0.21100	ND	0.01500	ND	0.0
13	ND	ND	0.36300	0.05067	0.02567	0.02200	0.0
14	ND	ND	0.35900	0.05233	0.02433	0.02233	ND
15	0.03275	ND	0.40733	ND	0.02800	ND	0.03
WHO(17)	0.1	0.01	3	-	2	0.07	0.3

Sample 1 =Gamato BH, Sample 2=Boqo BH ,Sample 3=Betemengist Reservoir 1, Sample 4=Betemengist Reservoir 2 , Sample 5= Dore bafano Reservoir, Sample 6=Dore tap 1 , Sample 7 =Dore bafano tap 2 , Sample 8 =Galo tap 1, Sample 9 =Galo tap 2 , Sample 10 =Umbulo Reservoir , Sample 11=umbulo tap , Sample 12=Jara reservoir , Sample 13 =Jara tap 1 , Sample 14 =Jara tap 2 and Sample 15 =Rukessa tap water.

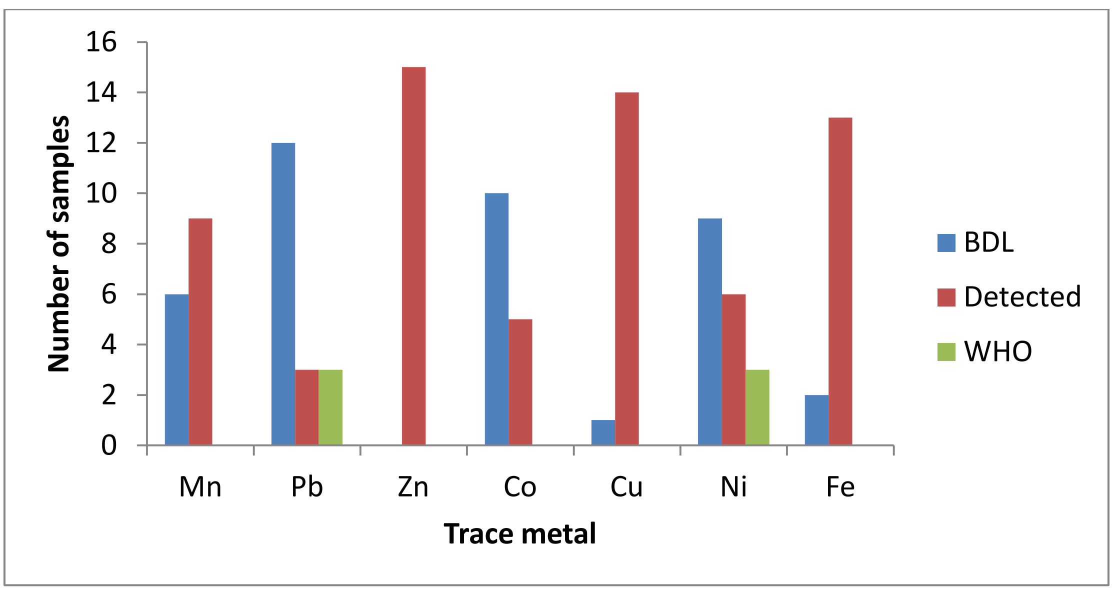

Figure 2: Status of different trace metals in drinking water samples of Hawassa Zuria Woreda, 2021

Lead was detected in 3 samples although in 12 samples, the concentration remained below the detection limit. The concentration of lead ranged from ND – 0.05567 mg L^{-1} with mean of 0.0077 mg/l. More than three-quarters of the samples are in the range of BDL values (below detection limit). The maximum level of lead was found in water sample from Umbulo tap with 0.05567 mg/L followed by in Boqo borehole with 0.0483 mg/L and in Gamato borehole with the concentration of 0.01167 mg/L.

Zinc was found in fifteen drinking water samples (Figure 2). Zinc concentrations ranged between 0.01633mg/l - 0.9499 mg/l. Highest (0.9499 mg/L) Zn concentrations were found in Dore reservoir. In the present analysis, the highest Zinc content was found in Galo tap 2 with the concentration of 0.9499mg/l and the lowest in sample from Dore tap 1 with the concentration of 0.01633mg/l.

Cobalt was detected only in 5 drinking water samples although in 10 samples it remained below the detection limit. In the present study, concentrations of cobalt ranged between ND – 0.06767mg/l. Copper was found in fourteen drinking water samples and only one water sample showed concentration of copper below the detection limit (Figure 2). Copper concentration ranged between 0.0051 mg/l – 0.04mg/l. Highest (0.04 mg/L) Cu concentrations were found in Jara Dado tap 1 and the lowest concentration was noted at Umbulo reservoir (0.00833mg/L).

In this study, Nickel was detected in 6 drinking water samples whereas 9 samples showed no concentration of Nickel (Figure 2). Nickel concentration ranged between ND - 0.0937mg/ with high concentration 0.0913 mg/l in Umbulo reservoir and 0.0937mg/L in Betemengist reservoir 2, respectively.

Iron was found in thirteen drinking water samples and only two water samples showed concentration of iron below the detection limit (Figure 2). Highest iron concentration was found in Umbulo reservoir followed by sample in Rukesa tap. The distribution of average metal concentrations in the drinking water was found in the order of Zn>Ni>Co>Cu>Mn>Fe> Pb.

Pearson Correlation Coefficient Matrix for Trace Elements and Physico-Chemical Characteristics

The correlation coefficient (r) was determined between lead, zinc, turbidity, copper and electric conductivity. Elemental pair Pb/Zn, ($r = 0.524$, $P < 0.05$) is significantly correlated with each other, whereas the rest of elemental pairs show no significant correlation with each other. Lead/turbidity ($r = 0.715$, $P < 0.01$) correlated with each other. Similarly, Cu/pH($r = 0.555$, $P < 0.05$) and Cu/Turbidity ($r = -0.522$, $P < 0.01$) significantly correlated with each other. Likewise, electric conductivity/turbidity ($r = 0.567$, $P < 0.05$) is significantly correlated with each other, whereas the rest are not significantly correlated (Table 5).

One sample t-test comparing the means of the parameters with WHO parametric values

Highly significant difference ($p<0.01$) was observed between the guideline values of WHO and manganese concentration measured in the collected samples. Lead concentration was not significant when compared to WHO guidelines value. Concentration of Zn showed significant difference when compared to the guideline value of WHO. Similarly, highly significant difference ($p<0.01$) was witnessed between the guideline value of Copper, Nickel and Iron (Table 6).

Table 5: Pearson correlation coefficient matrix for trace elements and physico-chemical characteristics in Hawassa Zuria Woreda (n =15).

	Mn	Pb	Zn	Co	Cu	Ni	Fe	EC	pH	Turb	HPI	HEI
Mn	1											
Pb	0.329	1										
Zn	0.080	**0.524***	1									
Co	0.262	0.079	-0.277	1								
Cu	-0.323	-0.395	0.078	-0.351	1							
Ni	0.163	-0.215	-0.483	0.281	-0.155	1						
Fe	0.310	0.343	0.407	-0.164	0.049	0.313	1					
EC	0.368	0.507	0.397	-0.292	-0.121	-0.243	.368	1				
pH	-0.184	-0.423	0.156	-0.167	**0.555***	-0.142	0.313	0.105	1			
Turb	-0.026	**0.715****	0.155	-0.067	**-0.522***	-0.144	0.040	**0.567***	-0.49	1		
HPI	0.275	**0.960****	0.451	0.029	-0.423	-0.077	0.321	0.017	-0.46	0.395	1	
HEI	0.461	**0.961****	0.438	0.155	-0.440	0.045	0.475	0.081	-0.44	0.356	**0.947****	1

***** Correlation is significant at the 0.05 level (2-tailed), HPI=Heavy metal pollution index, HEI=Heavy metal evaluation index; ** Correlation is significant at the 0.01 level (2-tailed)

Table 6: One sample t-test comparing the means of the parameters with WHO parametric values

Parameters	WHO (2017) guideline	N	Mean	SE	95% CI Lower	95% CI Upper	t.value
Mn	0.1	9	0.017	0.0048	-0.093	-0.073	-17.30**
Pb	0.01	3	0.0077	0.0047	-0.0078	0.0078	-0.485
Zn	3	15	0.306	0.058	-2.818	-2.569	-46.41**
Co	-	5	-	-	-	-	-
Cu	2	14	0.0168	0.0026	-1.988	-1.9776	-761.0**
Ni	0.07	6	0.0272	0.0085	-0.691	-0.655	-79.20**
Fe	0.3	13	0.0089	0.0038	-0.299	-0.283	-76.42**

Heavy Metals Contamination Factor (Cf)

Calculated values of pollution index for Mn, Zn, Fe and Cu were well below 1, which implies that the water samples were not polluted and are safe for drinking, whereas pollution index for both Pb and Ni above unity was calculated for six out of the fifteen samples indicating lead and Nickel contamination (Table 7).

Table 7: Pollution index for the fifteen sampling points

Sample	Mn(mg/l)	Pb(mg/l)	Zn(mg/l)	Fe(mg/l)	Cu(mg/l)	Ni(mg/l)
1	0.302	**1.167**	0.055	0.0033	0.0026	0.3
2	0.31	**4.833**	0.068	0	0.0026	0.357
3	ND	ND	0.021	0	0.006	0.343
4	0.393	ND	0.005	0.016667	0.0032	**1.338**
5	0.212	ND	0.157	0	0.0029	ND
6	0.031	ND	0.139	ND	0.0078	ND
7	ND	ND	0.085	0	0.02	ND
8	ND	ND	0.048	0	0.007	**1.009**
9	0.057	ND	0.081	0	0.011	0.576
10	0.012	ND	0.102	0.144	0.011	**1.305**
11	0.303	**5.567**	0.322	0.111	0.0055	ND
12	ND	ND	0.070	0	0.0075	ND
13	ND	ND	0.121	0	0.0128	0.031
14	ND	ND	0.119	ND	0.012	0.319
15	0.328	ND	0.136	0.1	0.014	ND
WHO(17)	0.1	0.01	3	0.3	2	0.07

Many sampling sites had low contamination factors category (Cf<1): Mn (100%), Pb (80%), Zn (100%), Fe (100%), Cu (100%) and Ni (80%). Some water samples had moderate contamination factor category (1≤Cf<3): Pb (6.7%) and Ni (20%). And some samples sites had considerable contamination factor category (3≤Cf<6): Pb (13.3%).

Heavy Metals Pollution Index (HPI)

Table 8 shows that mean HPI and HEI were 75.72 and 1.47, respectively. The mean HPI value did not surpass the critical value of 100. Twenty percent of the water samples had HPI values greater than the critical value of 100, with 50% of the borehole water and 25% of the tap water above the critical value. Based on HEI values, 100% of the water samples were classified as low in contamination (Table 8).

Table 8: Heavy metal pollution assessment for the fifteen sampling points

Serial no	Sample	HPI	HEI
1	Gamato BH	96.55	1.83
2	Boqo BH	382.34	5.57
3	Betemengist Reservoir 1	3.82	0.37
4	Betemengist Reservoir 2	18.12	1.81
5	Dore bafano reservoir	1.69	0.37
6	Dore tap 1	0.27	0.17
7	Dore bafano tap 2	0.011	0.11
8	Galo tap 1	160.31	1.064
9	Galo tap 2	10.83	1.23
10	Umbulo reservoir	15.79	1.667
11	Umbulo tap	436.09	6.30
12	Jara reservoir	0.021	0.078
13	Jara tap 1	3.53	0.45
14	Jara tap 2	3.58	0.45
15	Rukesa tap	2.85	0.578
	Min	0.01	0.08
	Max	436.09	6.30
	Mean	75.72	1.47

Discussion

In this study, manganese concentration ranged between ND - 0.05650mg/l. The manganese concentrations obtained was below the permissible limit (0.1mg/l) of WHO standard (WHO, 2017).The manganese concentrations in the current study were greater than in prior Ethiopian studies (9, 27). However, it was lower than Rawalakot's drinking water, which ranged from 0.54 to 4.73 mg/L (31) and Muzaffarabad's, which ranged from 0.031 to 0.246 mg/L(32). Human exposure to higher amount of manganese can result in severe disorders in nervous system, and long term exposure in its worst condition can cause permanent neurological effects with symptoms characterized by “Parkinson's disease” which include weakness, shaking, slowness, anxiety, quieter speech, depression, amnesia and frequent urination(17). The presence of manganese in drinking-water may lead to the accumulation of deposits in the distribution system. Oxidation and filtration are usually capable to achieve a manganese concentration of 0.05 mg/l in drinking-water.

The concentration of lead ranged from ND – 0.05567 mg L^{-1} with mean of 0.0077 mg/l. The maximum level of lead was found in water sample (Umbulo tap) with 0.05567 mg/L, which was higher than maximum allowable limit (0.01 mg/L (WHO, 2017). Higher concentrations of lead were recorded in sampling stations of Gamato borehole, Boqo borehole and Umbulo tap which were 0.01167mg/L, 0.04833mg/L and 0.05567mg/L, respectively. The current study's lead values were greater than the previous study, which ranged from 0.0003 to 0.0025 mg/L(33). However, this is lower than the recorded ranges in Muzaffarabad (0.0290.665 mg/L) (32) and Asgede Tsimbila District (0.008 to 1.10 mg/L)(26). The highest concentration may be due to domestic sewage, plumbing, piping used for the water distribution system and extensive agriculture practices in the study area. Prolonged exposure of lead at concentration above 0.01 in drinking water has adverse effect on central nervous system, blood cell and may cause brain damage(34, 35). This damage commonly leads to behavior and learning problems (such as hyperactivity), memory and concentration problems, high vital sign, hearing problems, headaches, slowed growth, reproductive problems in men and women, digestive problems, muscle and joint pain (36). Children are the foremost sensitive to Pb toxicity; it may cause behavioral disturbances, memory problems, and anemia.

Zinc concentrations ranged between 0.01633mg/l - 0.9499 mg/l. Highest (0.9499 mg/L) Zn concentration was found in Dore reservoir, which was below allowable limit (3 mg/L) (WHO,2017). In the present analysis, the highest Zinc content was found in Galo tap 2 with the concentration of 0.9499mg/l and the lowest in sample from Dore tap 1 with the concentration of 0.01633mg/l, which are lower than that of standard values set by Ethiopian standard agency (2013). Therefore, the drinking water of these areas has not satisfied the minimum need of Zinc content in our human body. Zinc concentrations in this location were found to be greater than those reported in the previous study (33, 37). The noted concentration of Zn in our study, 0.01633mg/l - 0.9499 mg/L, is comparable with results from Rawalakot city (0.56 to 2.69 mg/L) (31), Muzaffarabad, Pakistan (0.05–0.405mg/L) (32) and Asgede Tsimbila District, Ethiopia (0.785 - 5.32mg/L) (26). Zinc is the important heavy metal that plays a vital role in the metabolic and physiological processes of many organisms, because Zn deficiency affects normal growth and bone development. Nevertheless, higher concentrations of Zn is unsuitable as the Zn salts cause an unpleasant taste, opalescence in alkaline waters and causes poisoning in human(26). The average daily intake of zinc of 5 – 22 mg stable with a recommended dietary allowance for adult men being 15 mg/day, adult women 12 mg/day, infants mixes 5 mg/day, and for adolescents 10 mg/day(38).

Cobalt values in the current study varied from 0 to 0.06767mg/l, which were greater than those reported in the previous study (39). Cobalt is rarely detected in drinking water, but has a low concentration in drinking water ranging from 0.0001 –0.005 mg/l (40). Cobalt ions biochemically substitute the Zinc ions and result in high blood pressures, renal damage and binding with the enzymes and leads to Itai-itai type of diseases(41).

Copper concentration ranged between 0.0051 mg/l – 0.04mg/l, which was within the limit of international standards (2 mg/L). Highest (0.04 mg/L) Cu concentrations were found in Jara dado tap 1 and the lowest concentration was noted at Umbulo reservoir (0.00833mg/L).The value obtained were higher than other studies conducted in other areas (27, 33, 42). It is essential element, for enzymes and formation of hemoglobin. However, at high concentration of copper may lead to neurological complications, hypertension and liver and kidney dysfunctions(43). No guideline is set by WHO (2017) for Copper content in drinking water.

Nickel concentration ranged between ND - 0.0937mg/ with high concentration of 0.0913 mg/l in Umbulo reservoir and 0.0937mg/L in Betemengist Reservoir 2. The finding of the present study in Umbulo reservoir was above the international standards limit (0.07 mg/L) (WHO, 2017). The Nickel concentrations in the present study were found to be higher than those reported in previous studies(24). These higher concentrations in water may be due to untreated urban sewage. The intake of Ni compounds at high dose can cause severe illness like heart problems. The primary source of nickel contamination in drinking water is the leaching from metals which are in touch with potable water.

Concentration of iron ranged from 0.0 to 0.4 mg/L. Highest iron concentration was found in samples from Umbulo Reservoir followed by sample from Rukesa tap. Iron is an abundantly-found element in the earth's crust, though present usually in minor concentrations in natural water (32). The formation of ferric precipitate makes drinking water objectionable. In the present study, iron concentration could be compared with results from Pakistan (0.096 to 0.718 mg/L) (32), from Asgede Tsimbila Distric (0.11- 1.3mg/L) (26) and from Kafta Humera Woreda, Tigray (0.3 – 1.86mg/L)(27). The distribution of average metal concentrations in the drinking water was found in the order of Zn>Ni>Co>Cu>Mn>Fe> Pb.

The pH values of all the drinking water samples are found to be in the range between 6.69 and 7.65. The WHO recommends that the pH of drinking water should be in the range 6.50–8.50 and all samples had pH values within this range. Water temperature obtained from the present study range from 20 to 26 ^{o} C which is considered lower compared to WHO and Ethiopian maximum permissible limit. The result noted in the present study is comparable to other studies reported within a range of 11.8 to 27.7 ^{o} C(25) , 21.6 to 24.7 °C(26) and 15 to 27^{o} c (9).

The values of electric conductivity recorded range from 468.67 to 809.33μS/cm. The conductivity measurements found in the current study for all locations are higher than the standard drinking water guideline value of 400 μS/cm quoted by WHO (2017). The higher amount of EC indicates the presence of high amount of dissolved inorganic substances in their ionized form and drinking water with high EC reduces yield potential and affects the quality of water. The result noted in the present study is comparable with other studies reported from various geographical areas where EC value ranged from 128 to 627 μS/cm (26) and from 148.5 to 932 μS/ cm (27).

The transparency of drinking water is an essential standard for understanding the water quality. The turbidity values range from 1.2 to 11.63 NTU (Nephelometric Turbidity Units). Some other study reported enhanced turbidity values (26, 28).

The value of TDS ranged between 281.2 to 485.60 mg/l. The TDS level of drinking water must to be <500mg/l. Correspondingly, all the samples have low TDS values when compared to the permissible limits for the drinking purpose. TDS level higher than 1000 mg/L is not suitable for consumption and the values higher than 1200 mg/L significantly affects the consumers(29). Higher TDS quantity is more toxic to aquatic organisms and enhances the risks of diabetic, hypertensive and renal problems(29). The finding of the present study was comparable with reported by Tamungang (30) and Ogoko(23).

The Pearson's correlation (r) is used to find a correlation between at least two continuous variables. The value for a Pearson's correlation can fall between 0.00 (no correlation) and 1.00 (perfect correlation). More precisely, it can be said that parameters showing $r > 0.7$ are considered to be strongly correlated, whereas when r features a value between 0.5 and 0.7, a moderate correlation is shown to exist (48).

Pearson's correlation between the assessment indices showed a strong positive correlation between HPI and HEI ($r = 0.947$; $P < 0.01$). Lead correlated strongly and positively with all the heavy metal pollution indices (HPI, $r = 0.960$; HEI, $r = 0.961$) ($P < 0.01$). The strong positive correlation of Pb with the two pollution indices (HPI and HEI) implicates Pb pollution as the major source of drinking water contamination in the study area. Thus, Pb contributed significantly to the heavy metals load in the water samples than all other metals analyzed. It was also responsible for the high levels of the pollution indices obtained for some of the different water sources in the area.

One sample t-test revealed that highly significant difference ($p<0.01$) was observed between the guideline values of WHO and manganese concentration measured in the collected samples. Lead concentration was not significant when compared to WHO guidelines value. Concentration of Zn showed significant difference when compared to the guideline value of WHO (2017). Similarly, highly significant difference ($p<0.01$) was witnessed between the guideline value of Copper, Nickel and Iron drinking water concentration found in the samples.

The mean HPI recorded in the study area was 75.72. The HPI results in this study are in line with the previous findings (49-51). But contrary to the finding of Regina et al. (2021) and Boateng et al. (2015) who reported HPI value greater than 100 of underground water from Ejisu-Juaben Municipality, Ghana and southwest coast of Ghana, respectively(46,52).

Conclusions

The water sample collected was tested for heavy metal (Mn, Pb, Zn, Co, Cu and Ni) and physical parameters such as temperature, pH, EC, TDS and turbidity of the ground water. Physicochemical parameters that surpassed these safe guidelines in different sampling sites were temperature, electric conductivity, lead and nickel.

Some heavy metals (Pb and Ni) in some water samples were higher than the international standard maximum allowable limits in sample sites S4, S8, and S10, which had Nickel concentration above the recommended limit. The high levels of lead at the study site (S1, S2, and S11) could be attributable to plumbing, water distribution system piping, and widespread agriculture practices. This may have a negative impact on human health. Pollution index ranged between not affected to moderately affected for whole samples sites. This moderate contamination factors is an indication of pollution hazards and poor drinking water treatment practices in the study area which, in turn, have implications on human health. The distribution of average metal concentrations in the drinking water was found in the order of Zn>Ni>Co>Cu>Mn>Pb.

This study strongly recommends that the authorized body pay special attention to physico-chemical approaches for removing nickel and lead from drinking water, such as chemical coagulation, chemical oxidation or reduction, active carbon adsorption, filtration, ion exchange, and membrane technologies.

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Ethical consideration

Ethical clearance and approval for this study was obtained from Hawassa University, College of Natural and Computational Science, Institutional Review Board (IRB). Then a permission letter from the University was obtained and submitted to Sidama Water Bureau. Similar letter written by the Regional Water Bureau (RWB) was given to to Hawassa Zuria Water Office (Dore Bafano).

Data Availability statement

All data supporting the findings of this study are available within the article.

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